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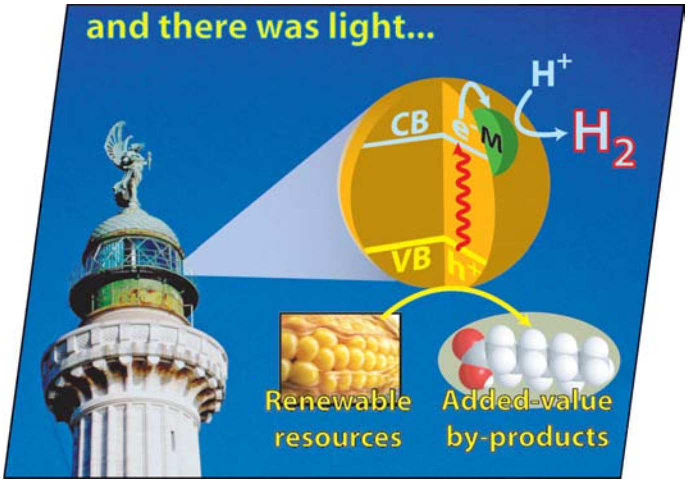
COVER PICTURE

The cover picture shows how light can be efficiently used to activate hydrogen production over metal oxides from biomass-derived compounds, such as alcohols and sugars. These processes have gained a considerable importance for the sustainable production of H_2, a strategic energy vector, starting from renewable resources. Interestingly, H_2 generation from these largely available raw materials is accompanied by the simultaneous formation of added-value by-products that might be appealing even for other applications. The Microreview by D. Barreca, P. Fornasiero et al. on p. 4309ff focuses on recent developments in the field, discussing selected representative research results and highlighting the major open problems and future perspectives.



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MICROREVIEW

Sustainable Chemistry

M. Cargnello, A. Gasparotto, V. Gombac, T. Montini, D. Barreca,* P. Fornasiero* **4309–4323**

Photocatalytic H_2 and Added-Value By-Products – The Role of Metal Oxide Systems in Their Synthesis from Oxygenates

Keywords: Hydrogen / Photoreforming / Metal oxides / Semiconductors / Biomass

Photoreforming of biomass-derived compounds holds a significant promise for the sustainable production of hydrogen, a strategic energy vector whose obtainment from renewable sources is currently in high demand. This review discusses the most important aspects of such processes, focusing on the oxygenates used and added-value by-products that are formed concomitantly to H_2 evolution.

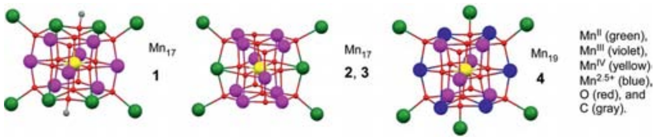
SHORT COMMUNICATION

Mixed-Valent Supercubanes

Y. Okui, F. A. Catusanu, R. Kubota, B. Kure, T. Nakajima, T. Tanase,* T. Kajiwara, M. Mikuriya, H. Miyasaka, M. Yamashita **4325–4330**

Systematic Expansion of Supercubane Cores in Manganese Oxo Clusters with Tricarboxylate Ligands

Keywords: Manganese / Carboxylate ligands / Mixed-valent compounds / Cluster compounds / Supercubane cores / Magnetic properties



A novel class of high-nuclearity Mn_{17} (**1**–**3**) and Mn_{19} (**4**) complexes including Mn_{13} supercubane cores are synthesized by utilizing Kemp's tricarboxylate ligands, in which the oxidation states of the Mn_{13} mineralomimetic units are systematically altered depending on their vertex face-capping ligands.

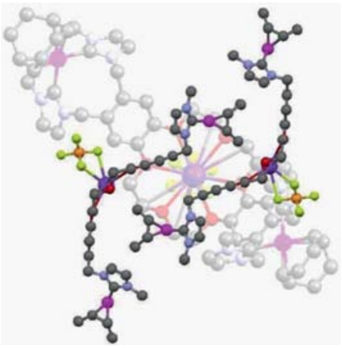
FULL PAPERS

NHC-Crown Ethers

S. Shrestha, C. Gimbert-Suriñach,* M. Bhadbhade, S. B. Colbran* **4331–4337**

Four Soft Donors and a Hard Centre: Rhodium Complexes of a Novel Tetrakis(NHC)-Encapsulated Crown Ether Ligand

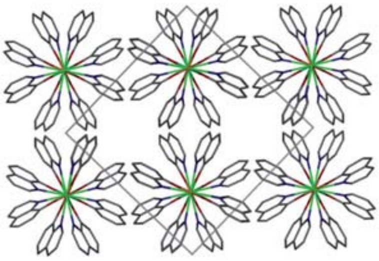
Keywords: Crown compounds / Carbenes / Nitrogen heterocycles / Rhodium / Alkali metals



A facile and versatile route to novel multinucleating ligands spanned by a crown ether centre is described. The methodology was used to prepare two new tetrakis(imidazolium)crown ether salts, precursors to $(NHC)_2Rh$ dimers spanned by a crown ether. The crown ether centre in the Rh dimers binds alkali metal ions. The crystal structure of a K^+ adduct is described.

Heterobimetallic Complexes

The heterobimetallic 1D-polymeric alkali metal/lanthanoid $[AMLn(Q)_4]_n$ (Q = OQ (8-quinolinolate): AM = Li, Ln = Tb, Ho, Er; AM = K, Ln = Er; Q = MQ (2-methyl-8-quinolinolate): AM = Rb; Ln = Tb, Er) complexes were obtained after rearrangement reactions between AM(Q) and $Ln(Q)_3$ in a 1,2,4,5-tetramethylbenzene flux at elevated temperatures.



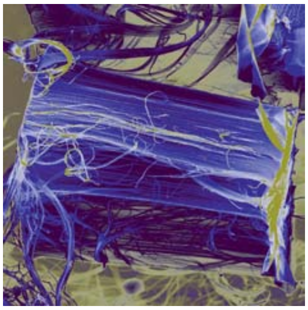
G. B. Deacon,* T. Dierkes, M. Hübner, P. C. Junk,* Y. Lorenz, A. Urbatsch **4338–4348**

Alkali Metal/Lanthanoid Heterobimetallic Complexes of 8-Hydroxyquinolines Accessed by Pseudo-Solid-State Reactions

Keywords: Lanthanides / Alkali metals / Quinolinolates / Heterometallic complexes / Metal–organic frameworks

Multiwall Carbon Nanotubes

The synthesis and electrochemical performance of stochastically arranged and 3D ordered CNT/$LiCoPO_4$ cathode composites is reported. Li ion extraction within such composites seems to be a two-step process and Li intercalation a one-step process, which highlights the enhanced kinetics of the Li insertion process in such composites compared to conventional carbon black/Li_xCoPO_4 composites.



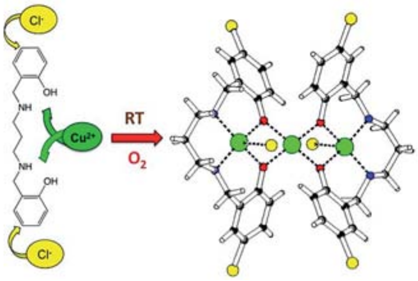
J. J. Schneider,* J. Khanderi, A. Popp, J. Engstler, H. Tempel, A. Sarapulova, N. N. Bramnik, D. Mikhailova, H. Ehrenberg, L. A. Schmitt, L. Dimesso, C. Förster, W. Jaegermann **4349–4359**

Hybrid Architectures from 3D Aligned Arrays of Multiwall Carbon Nanotubes and Nanoparticulate $LiCoPO_4$: Synthesis, Properties and Evaluation of Their Electrochemical Performance as Cathode Materials in Lithium Ion Batteries

Keywords: Hybrid materials / Lithium-ion batteries / Electrochemistry / Nanotubes / Nanoparticles / Phosphoolevins

Oxidative Halogenation

The selective copper-mediated halogenation of the aromatic rings of saltren-type ligands can be obtained under extremely mild conditions: the simple aerobic reaction of the ligand with $CuCl_2$ or $CuBr_2$ at room temperature in acetonitrile leads to the formation of a trinuclear copper complex exhibiting halogenated ligands.



I. Gamba, P. Gamez, E. Monzani, L. Casella, I. Mutikainen, J. Reedijk* **4360–4368**

Selective Copper-Mediated Halogenation of Aromatic Rings Under Mild Conditions

Keywords: Oxidation / Copper / Ring Closure / Halogenation

MOF Catalysis

A family of isostructural MOFs, $[Ln_2(pda)_3(H_2O)]\cdot 2H_2O$, possess 3D honeycomb-shaped networks with 1D channels, which accommodate guest and coordinated water molecules. Activated $[Tb_2(pda)_3]$ exhibits excellent catalytic performance in the heterogeneous acetalization of benzaldehyde with methanol. Easy recycling makes this catalyst a highly promising candidate to address environmental concerns.

Y.-w. Ren, J.-x. Liang, J.-x. Lu, B.-w. Cai, D.-b. Shi, C.-r. Qi, H.-f. Jiang,* J. Chen, D. Zeng **4369–4376**

1,4-Phenylenediacetate-Based Ln MOFs – Synthesis, Structures, Luminescence, and Catalytic Activity

Keywords: Metal-organic frameworks / Heterogeneous catalysis / Lanthanides / Luminescence

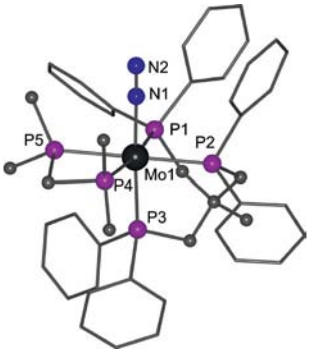
CONTENTS

Activation of Nitrogen in Mo Complexes

J. Krahmer, H. Broda, C. Näther, G. Peters, W. Thimm, F. Tuczek* **4377–4386**

Octahedral Molybdenum(0) Monodinitrogen Complexes Facially Coordinated by the Tripodal Ligand 1,1,1-Tris(diphenylphosphanylmethyl)ethane – Influence of Diphosphane Coligands on the Activation of N_2

Keywords: Molybdenum / Nitrogen / P ligands / Nitrogen fixation / Tripodal ligands



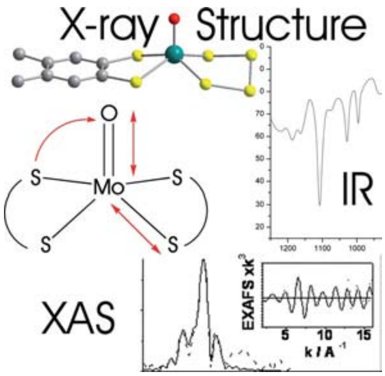
Two molybdenum dinitrogen complexes are reported, $[Mo(N_2)(tdppme)(dmpm)]$ (**2**) and $[Mo(N_2)(tdppme)(dppm)]$ (**3**). Complexes **2** and **3** are facially coordinated by the tripodal ligand 1,1,1-tris(diphenylphosphanylmethyl)ethane and contain bidentate coligands dimethylphosphanylmethane and diphenylphosphanylmethane, respectively. Importantly, **2** can be protonated to the NNH_2 complex $[Mo(NNH_2)(tdppme)(dmpm)](OTf)_2$.

Bioinorganic Chemistry

P. P. Samuel, S. Horn, A. Döring, K. G. V. Havelius, S. Reschke, S. Leimkühler, M. Haumann,* C. Schulzke* **4387–4399**

A Crystallographic and Mo K-Edge XAS Study of Molybdenum Oxo Bis-, Mono-, and Non-Dithiolene Complexes – First-Sphere Coordination Geometry and Noninnocence of Ligands

Keywords: Molybdenum / Enzyme models / X-ray absorption spectroscopy / Noninnocence / Bioinorganic chemistry



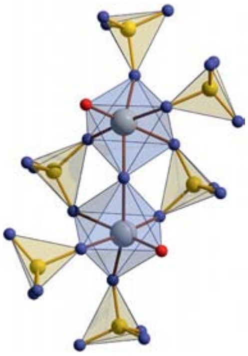
Ten molybdenum complexes, modeling the dimethyl sulfoxide reductase family of molybdenum-dependent enzymes, were investigated by X-ray absorption spectroscopy and their structures were evaluated in detail by using additional crystallographic data. Comparison with enzyme data revealed that the active site geometry is dominated by molybdenum, and X-ray absorption data correlates well with IR data.

Refractory Metal Sulfates

U. Betke, M. S. Wickleder* **4400–4413**

Oleum and Sulfuric Acid as Reaction Media: Structural Features and Thermal Behavior of $RE_2[W_2O_3(SO_4)_6]$ (RE = Sm–Gd, Ho), $RE_2Nb_2O_2(SO_4)_3[H(SO_4)_2]_2$ (RE = Y, Ce–Nd, Sm–Er), $Sm_2Nb_2O_2(SO_4)_5(S_2O_7)$, and $M_2Nb_4O_5(SO_4)_8$ (M = Bi, Eu)

Keywords: Rare Earths / Niobium / Tungsten / Refractory metals / Sulfates / Thermal decomposition



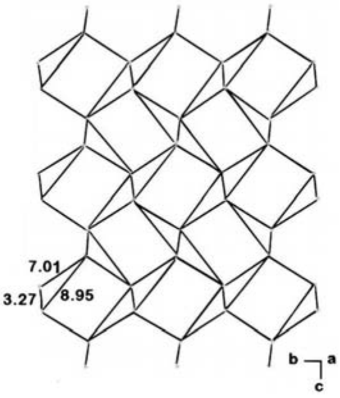
Mixtures of H_2SO_4 and SO_3 turned out to be versatile media for the preparation of complex sulfates containing refractory metals and lanthanides. These sulfates exhibit unique structural features and show a thermal behavior that is in part influenced by strong hydrogen bonding observed in the structures.

Spin–Liquids

O. Piovesana,* B. Chiari, A. Cinti, A. Sulpice **4414–4420**

Synthesis, Structure, and Magnetic Properties of $Cu_2L_2Cl_2$ (LH = *N*-Salicylidene-1,2-ethanediamine) – A New $S = 1/2$ Spin–Liquid Candidate

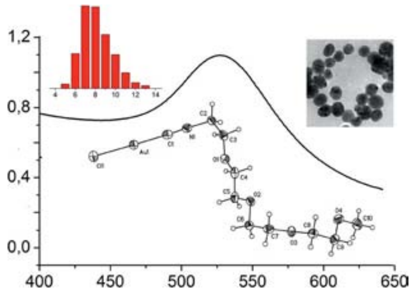
Keywords: Copper / Spin–liquids / Magnetic properties



The new compound $Cu_2L_2Cl_2$ (LH = *N*-salicylidene-1,2-ethanediamine) behaves as a pure spin $S = 1/2$ paramagnet down to 1.7 K, despite a fully ordered structure where dichloro-bridged binuclear units are connected by weak H bonds. This persisting spin disorder is tentatively explained by a 3D spin Hamiltonian where exchange interactions of opposite signs form a macroscopic degenerate spin–liquid state.

Gold Nanoparticles

Ethylene glycol isocyanide gold chlorides with different chain lengths [AuCl{C≡N-(CH$_2$CH$_2$O)$_n$CH$_3$}] (n = 1, 3, 4) were prepared and used in the generation of gold nanoparticles in different solvents without the addition of any further stabilizing agents. Nanoparticle sizes between 6.4 and 27.2 nm were obtained.



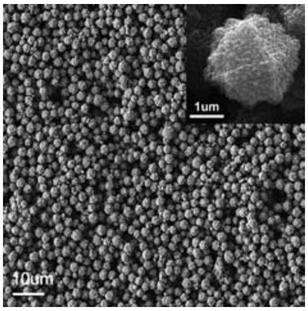
**A. Tuchscherer, D. Schaarschmidt,
S. Schulze, M. Hietschold,
H. Lang* 4421–4428**

Simple and Efficient: Ethylene Glycol Isonitrile Gold(I) Chlorides for the Formation and Stabilization of Gold Nanoparticles

Keywords: Nanoparticles / Gold / Isonitriles / Ethylene glycol / Redox chemistry

Hierarchical Microparticles

Uniform hierarchical durian-shaped dodecahedral rutile microparticles have been grown by hydrothermal synthesis with oxalic acid. It is suggested that the hierarchical structure is epitaxially grown from a precursor (i.e., titanium oxide oxalate hydroxide hydrate) due to their structural resemblance of the arrangement of corner-shared TiO$_6$ octahedrons.



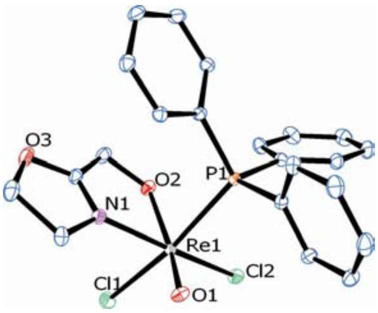
**J. Liu, X. Yang, Y. Wen, Q. Gao,
Q. Zhou, C. Liang, M. Wu* ... 4429–4433**

Hierarchical Durian-Shaped Dodecahedral Rutile Microparticles

Keywords: Nanostructures / Hydrothermal synthesis / Titanium / Rutile / Hierarchical structures

Epoxidation Catalysis

Oxidorhenium(V) complexes containing oxazolinylmethoxido ligands were synthesized and characterized by spectroscopic means and X-ray crystallography. The complexes are air- and moisture-stable and show activity for the epoxidation of cyclooctene.



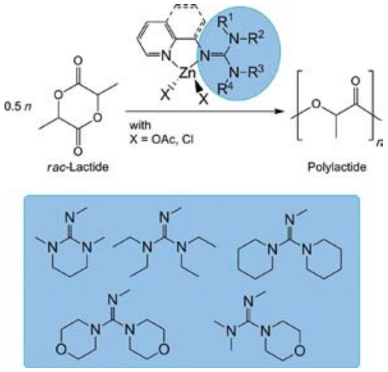
**B. Terfassa, P. Traar, M. Volpe,
N. C. Mösch-Zanetti,* V. J. T. Raju,
N. Megersa, N. Retta 4434–4440**

Oxidorhenium(V) Complexes with Oxazolinylmethoxido Ligands – Structure and Catalytic Epoxidation

Keywords: Rhenium / Oxazoline / Epoxidation / Oxidation

Lactide Polymerisation

The synthesis and molecular structures of zinc complexes of two series of new guanidine–pyridine hybrid ligands are reported. The complexes were proven to be active and stable catalysts in the melt polymerisation of D,L-lactide. The influence of the guanidine unit and coligands on the polymerisation activity was examined.



**J. Börner, I. dos Santos Vieira,
M. D. Jones, A. Döring, D. Kuckling,
U. Flörke, S. Herres-Pawlis* ... 4441–4456**

Zinc Complexes with Guanidine–Pyridine Hybrid Ligands – Guanidine Effect and Catalytic Activity

Keywords: Sustainable chemistry / Zinc / Polymerization / Polymers / Biodegradable polymers / Ring-opening polymerization / Density functional calculations

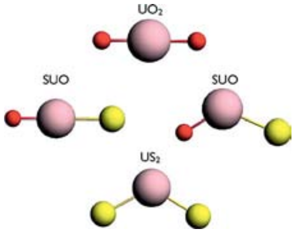
CONTENTS

Uraniun Sulfides

L. Andrews, X. Wang, B. Liang,
F. Ruipérez, I. Infante,* A. D. Raw,
J. A. Ibers 4457–4463

Matrix Infrared Spectroscopy and a Theoretical Investigation of SUO and US_2

Keywords: Uranium / Matrix isolation / Density functional calculations / Energy decomposition



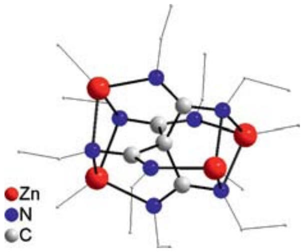
Laser ablation and matrix isolation spectroscopy have been used to produce US_2 and SUO molecules in solid argon. The asymmetric stretching mode of US_2 is found at 438.7 cm^{-1}, and the SUO molecule exhibits a U–O stretching mode at 857.1 cm^{-1}. Density functional and CASPT2 calculations have been used to corroborate the experiments and analyze the structures of these molecules.

Carbodiimide Chemistry

S. Schmidt, B. Gutschank,
S. Schulz,* D. Bläser, R. Boese,
C. Wölper 4464–4470

Synthesis and X-ray Crystal Structures of Multinuclear Zinc Amidinate Complexes

Keywords: N ligands / Zinc / X-ray diffraction



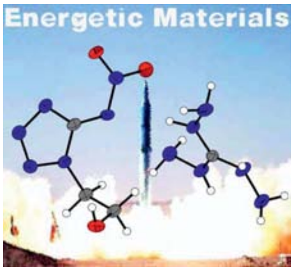
C–C bond formation reactions between $ZnMe_2$ and carbodiimides were investigated. The formation of Lewis acid–base adducts of a tetranuclear zinc amidinate complex was also studied.

Energetic Materials Research

N. Fischer, T. M. Klapötke,*
J. Stierstorfer 4471–4480

Energetic Nitrogen-Rich Salts of 1-(2-Hydroxyethyl)-5-nitriminotetrazole

Keywords: Nitrogen / Nitrogen heterocycles / Energetic materials / Explosives



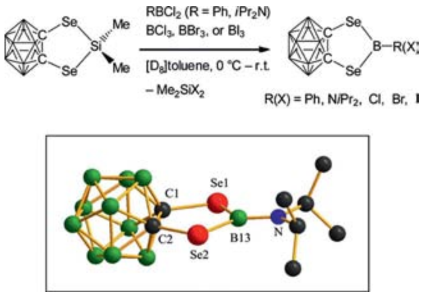
Future energetic materials should be high performing, insensitive, and low in toxicity. The taming of nitriminotetrazoles with alkyl side chains and nitrogen-rich salt formation led to a new class of insensitive explosives.

Diselenaborolanes

B. Wrackmeyer,* E. V. Klimkina,
W. Milius 4481–4492

1,3,2-Diselenaborolanes with an Annelated Dicarba-*closo*-dodecaborane(12) Unit: Synthesis, Molecular Structure and Reactivity

Keywords: Main group elements / Carboranes / Boron / Selenium / Heterocycles / Density functional calculations / Multinuclear NMR spectroscopy



Cleavage of Si–Se bonds with boron trihalides (BCl_3, BBr_3, BI_3) and dichlorides ($PhBCl_2$, iPr_2NBCl_2) affords the 1,3,2-diselenaborolanes in essentially quantitative yield. NMR spectroscopic studies (^{1}H, ^{11}B, ^{13}C, ^{29}Si, ^{77}Se) and two X-ray structural analyses, together with calculations of NMR parameters using DFT hybrid methods [RB3LYP/6-311+G(d.p) level of theory] complete the characterization.

* Author to whom correspondence should be addressed.

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